



Audio jack based miniaturized mobile phone electrochemical sensing platform



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ABSTRACT

We demonstrated a mobile phone sensing platform, MoboSens, with integrated plug-n-play microelectronic ionic sensor that performs electrochemical measurement by using audio jack of a smartphone. This platform was used to measure nitrate concentration using few microliter liquid samples on field along with providing geospatial map locations through wireless network. This compact MoboSens platform (~65 g) based on smartphone is able to detect nitrate concentration in water with a limit of detection of 0.2 ppm within 1 min. The nitrate ion detection on MoboSens platform is performed by a microfabricated microfluidic sensor utilizing cyclic voltammetry based electrochemical process. The stability of the measurements was verified by performing the experiments under varying temperature, pH and ion interference conditions. The mobile phone app reports the quantitative nitrate sensing results along with user's input metadata. The results can be automatically saved on secure cloud servers or can be pushed on public social media, e.g. Twitter. Finally, the digital sensing information can be retrieved with geospatial information tagged on an internet map service, e.g. Bing Map for public sharing and viewing. We tested this lab-on-a-chip mobile sensing platform for field water quality measurement and confirmed our mobile sensing results with other existing analytical testing methods.

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1. Introduction

Even though nitrogen is a vital part of living organisms such as amino acids, proteins and nucleic acids (DNA), excessive nitrogen has adverse health and environmental impact [1]. In US, EPA (Environmental Protection Association) regulates the maximum allowable contamination level for nitrate as nitrogen ($\text{NO}_3\text{-N}$) to be 10 ppm (10 mg/L) so as to prevent adverse health effect on population [2]. Nitrite (NO_2^-), a reduced form of nitrate, is also a major cause of poisoning in fish and is toxic to human health as well. Therefore, the effective and accurate detection of nitrate concentration has become significant and necessary.

Currently citizens are not equipped to detect invisible contaminants in water as it requires specialized instrument, certain level of expertise and is associated with high cost (equipments and chemicals) to measure them. In addition to general public, people such as environmentalists, tourists and farm owners are likely to determine the water contamination often. So an easy to operate, low-cost and portable platform for nitrate detection is an unmet need. Moreover, a nitrate sensor operated by a mobile phone platform will be quite helpful in achieving mapped information of contaminant, since such information come with location and temperature information. Also, these data can be sent to social platform normally connected to cloud server for wider dissemination.

Many existing methods such as spectroscopic, chromatography, capillary electrophoresis and electrochemistry, are available to determine nitrate concentration [3]. Spectroscopic method is broadly used for nitrate determination, mainly using UV/Vis or fluorimetric emission [4]. This method normally involves the use of chemical reactions like Griess reaction to form highly fluorescent compounds to be compared and measured using a

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spectrophotometer [5–7]. The detection limit achievable by this method is in between 0.28 ppb and 28 ppb [3]. But multiple reaction steps make this method time consuming; also the instrument for fluorescence spectroscopic detection is not accessible to common citizens. Chromatography method, either gas chromatography or ion chromatography, is also commonly used in laboratory setups [8–11]. Although the process is accurate, some experiment requirements like high pressure for HPLC (high-pressure liquid chromatography) and long column (200 mm) [9] makes it difficult to be miniaturized. The flow rate control of mobile phase is also sensitive to vibration or trembling and hence unsuitable for a portable device. Further, due to the associated high cost and large form factor, it is unlikely to be adopted by regular citizen for routine nitrate measurements. For capillary electrophoresis method, the column used is even longer and the set up for fluorescence detection is complicated [12,13].

Compared with other methods, electrochemistry method is relatively easy to operate and can be transformed to a portable platform [3]. In electrochemical methods, due to the application of voltage potential between reference and working electrodes, oxidation or reduction of electro-active species happens [14]. Cyclic voltammetry is a popular method often used in electrochemistry systems [1,15,16] because of its ease of data interpretation. Miniaturized or microscale electrodes along with microfluidic integration greatly reduce the required liquid sample volume and will make the whole package portable [17].

Here we presented a lab-on-a-chip mobile sensing system (MoboSens), which includes a miniaturized electrochemical sensor, mobile phone platform (mobile phone application and controlling circuit) to control the sensor and microfluidics to handle the liquid samples. The use of miniaturized electrode has several advantages such as low ohmic drop, low capacitive current, small time constant and fast mass transport. [18,19] A user-friendly mobile application interface is developed which enables a simple and easy to use testing procedure. Due to its lightweight (~65 g) and small form factor, the whole system is portable. Unlike some smartphone based sensing platforms developed previously [20,21], our platform makes use of audio jack as the sensing interface instead of camera. The embedded camera on smartphone enables people to do image or spectrum analysis in the mobile application [22–25], but the application is limited only to “retrieving” signal. The use of audio jack can break through this one-way communication by setting a mechanism which will both “send” and “retrieve” signals, just like the way people listen to the music and record a voice. The use of micro USB interface to perform electrochemical testing was made previously, but this could not achieve cross-platform testing easily because of the different protocol for different smartphones like Samsung (Android system) and iPhone (iOS system) [26]. In addition, audio jack has been used to generate voltage excitation signal for electrochemiluminescence detection [27]. However, it suffers from cross-platform compatibility problem since the voltage value generated from audio jack varies among different phones. Instead, what we generated and received from audio jack is not the volume of sound but the tone frequency, which can break through this cross-platform limitation. This enables us to do different electrochemical testing by generating smooth waveforms. Recently, audio jack was also used to send control signal from phone to an external integrated potentiostat to perform different electrochemical tests [28]. In contrast, by making use of the CPU, ADC and DAC from phone itself, instead of external electronic components, we are able to minimize the form factor and cost (~\$10) of our package to achieve one hand-held platform to do electrochemical testing. Currently, the smartphone based system is designed for nitrate concentration measurement. Further development of the sensor is underway to include detection of other ions like phosphate or microbial contaminants like bacteria [29].

2. Experimental methods

2.1. Design of MoboSens system

The schematic model of MoboSens is shown in Fig. 1(a) and (b). A photograph of the complete package of MoboSens including the microfluidics, mobile apps and the controlling circuits is shown in Fig. 1(c). Due to its uniformity in design and availability in all mobile phones, we decided to use the audio jack for the electrical signal input and output of the MoboSens system (instead of the USB port). Fig. 2 shows the component level description of the MoboSens system. The sequence of events during the detection of nitrate using MoboSens are as follows: the sweep voltage required for driving the nitrate electrochemical sensor is first generated by the speaker D/A module in the mobile phone. The output voltage from the sensor is simultaneously retrieved by the A/D module embedded in microphone. In order to achieve frequency match between mobile phone and nitrate sensor, a circuit board with modulation and demodulation components is added to the MoboSens system.

A software platform in mobile phone is developed to drive and retrieve the data from the nitrate sensor. There is an option to perform real-time calibration or to use stored calibration curve for the nitrate measurements. The calibration measurements are performed using standard nitrate solutions with different concentrations. Finally, after measurements of the nitrate concentration of field water samples, the results can be shared (on social network like Twitter) or stored in remote server (for example, cloud server) for further analysis along with the information of geographical location (latitude and longitude), temperature and user inputs (meta data). The schematic of the entire system is shown in Fig. 2.

2.2. Sensor microfabrication

The miniaturized nitrate sensor is fabricated on glass substrate. The layout and image of sensor are shown in Fig. 3(a) and (b). The electrodes are designed in a circular fashion to enable uniformity in the current flow in the electrochemical system. The surface area of counter, working and reference electrode are $9.05 \times 10^{-4} \text{ cm}^2$, $7.05 \times 10^{-4} \text{ cm}^2$ and $3.47 \times 10^{-4} \text{ cm}^2$, respectively. The area of counter electrode is designed to be the largest for preventing oxygen-bubble formation on its surface due to OH^- oxidation at high current density [18]. The schematic of fabrication process is described in detail in Fig. 3(c). We first patterned the counter electrode by optical lithography and deposited 200 nm gold by electron beam (e-beam) evaporation. After lifting off with acetone, the gold inside counter electrode region will be left. With the same method another layer of silver (200 nm) is fabricated as reference and working electrodes. Ag/AgCl is usually used as reference electrode, but it may also provide chloride contamination during nitrate detection. Instead, silver is used as reference electrode due to its simplicity in fabrication and sufficient stable potential in 0.1 M NaOH electrolyte [18]. It has been reported that silver has high sensitivity for reducing nitrate ions in alkaline environment [30,31]. Although copper electrode also shows this good property in acidic solution [32,33], it was found to dissolve during the reduction of nitrate [32]. That's why we chose silver as working electrode here. For better adhesion on glass, one layer of titanium (20 nm) instead of chromium was deposited before gold and silver evaporation because chromium adhesion layer severely corrode during electrochemical activation process [18]. In order to minimize uncompensated resistance (R_u) between reference and working electrodes, these two electrodes are kept at close distance (10 μm) to increase accuracy. As an advantage of miniaturized electrode, this will directly result in much smaller cell time constant, which is the product of R_u and double-layer

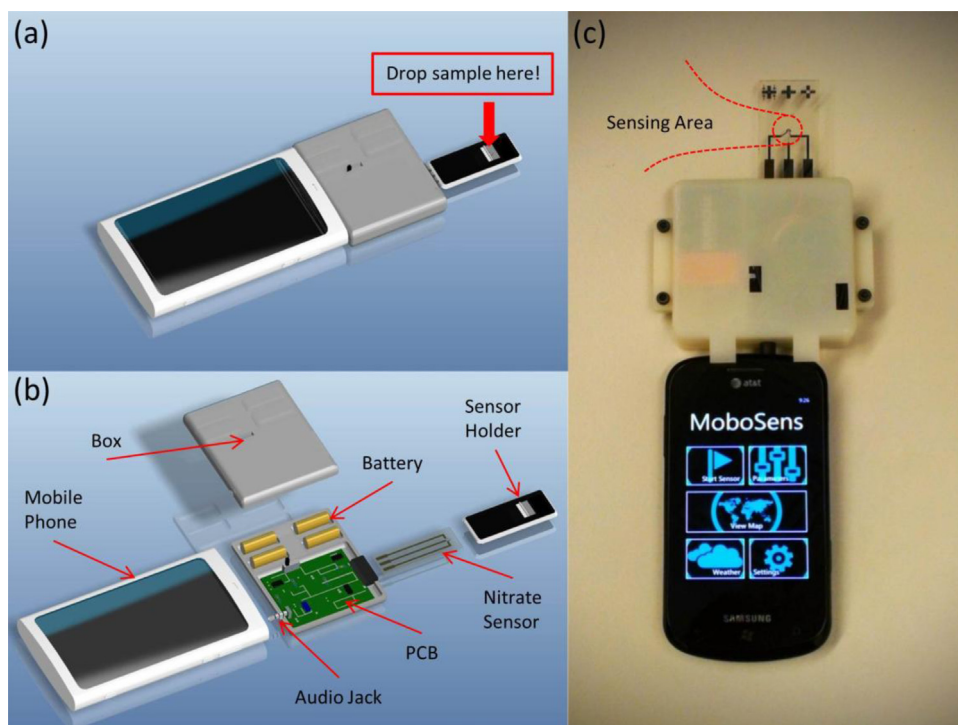


Fig. 1. Concept design and real package of MoboSens. (a) Assembly view of MoboSens. (b) Detailed components of MoboSens. (c) Photograph showing the complete MoboSens system.

capacitance (C_d). Smaller cell time constant leads to the lower limit of experimental time scale.

2.3. Cyclic voltammetry method

Cyclic voltammetry method is used to obtain the reduction/oxidation reaction in the electrochemical system. The voltage sweeping range available for MoboSens is -1.6 V to $+1.5\text{ V}$. Sodium

hydroxide (NaOH) is used as electrolyte and sodium nitrate with different concentrations is added to the electrolyte for testing. The concentration of electrolyte (NaOH) is made to be 100 mM to eliminate the contribution of migration to the mass transfer of electro active species. The potential of hydrogen evolution will also be pushed to more negative value at such alkaline environment [34]. The electrodes are first activated by sweeping the potential from -1.5 V to 1.0 V for 20 cycles (scan rate 1 V/s) with final potential

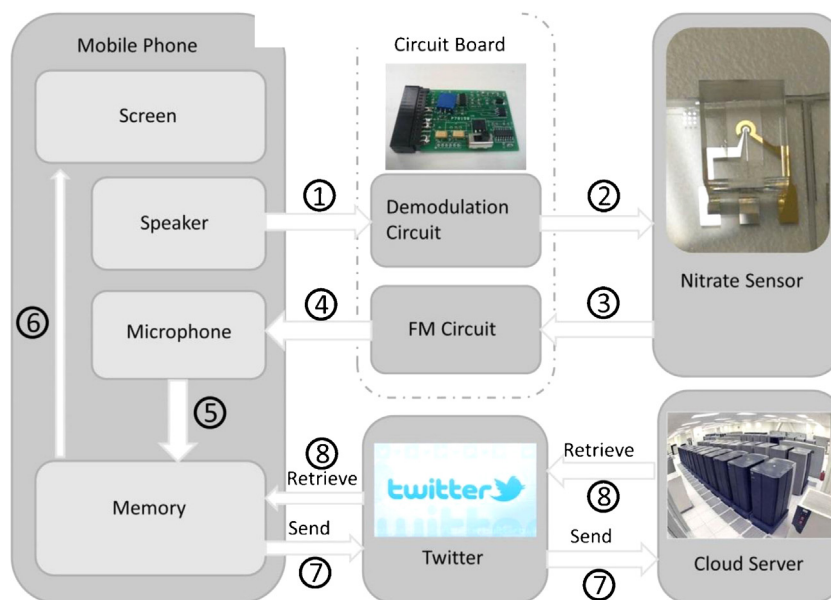


Fig. 2. Schematic of operation of MoboSens system. (1) Signal with changing frequency is generated from speaker to demodulation unit. (2) Signal was demodulated to sweeping voltage for cyclic voltammetry testing. (3) The output current from miniaturized sensor was transformed to voltage and sent to frequency modulation unit. (4) Output signal from sensor was modulated to send to microphone. (5) "Recorded" raw data was transformed to frequency and analyzed in memory. (6) Frequency vs time plot was shown on mobile screen. (7) Analyzed results were sent to social platform (like Twitter) and stored by cloud server. (8) Information from cloud server or social platform could also be retrieved to smart phone for analysis.

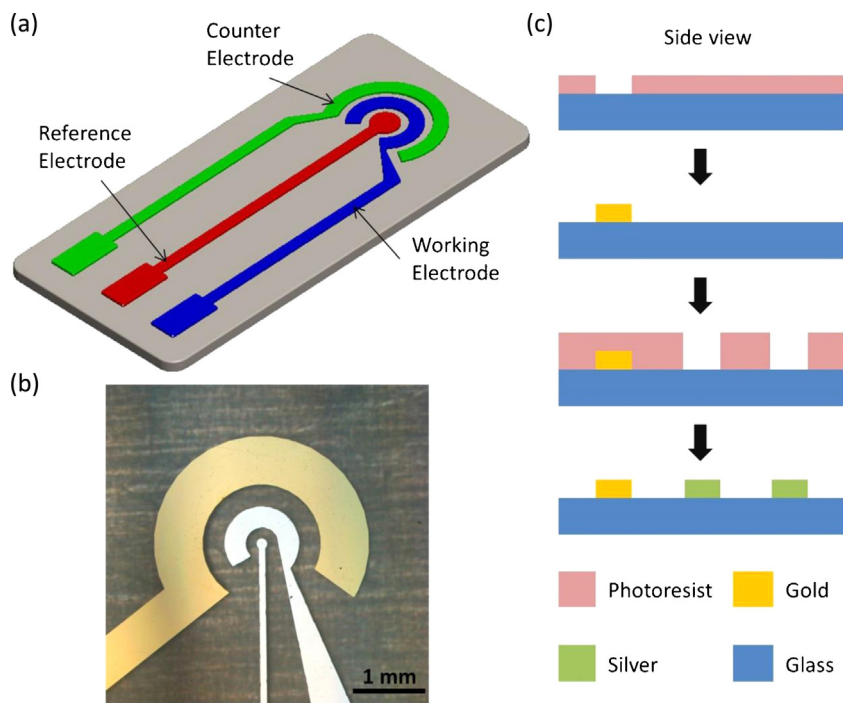


Fig. 3. Sensor electrodes and fabrication process. (a) Schematic showing the three-electrode electrochemical sensor utilized in the MoboSens. (b) Optical image of the fabricated sensor electrodes. (c) Schematic showing the fabrication process involving series of photolithography and lift off to fabricate the electrochemical miniaturized sensor.

at -1.5 V. This activation process will remove the possible oxidation layer at the surface of working electrode [20,21,35]. In order to avoid oxidation of silver working electrode and to make nitrate reduction happen, the sweeping voltage between working and reference electrode is chosen from 0 V to -1.5 V with a sweeping rate of 100 mV/s for cyclic voltammetry testing. This sweeping rate guarantees only 30 s for one cycle measurement without severe distortion which normally occurs at high sweeping rate due to extra charging current from double-layer capacitance. We start from the cathodic sweeping because the reversal process is always less precise by referencing forward process which is uncertain in folded Faradaic response [19]. The reduction peak of nitrate will be detected when sweeping toward -1.5 V. The whole testing involved 4 cycles and the data from the fourth cycle was used for calculation as the reduction peaks were stabilized in roughly 3 cycles.

2.4. Design of circuit board

Since there is a frequency limitation (which must be greater than 20 Hz) for input and output signals from both mobile phone audio jack and microphone, a sine wave at constant amplitude with frequency increasing from 5300 Hz to 7600 Hz and decreasing from 7600 Hz to 5300 Hz is generated from mobile phone audio jack. 5300 Hz is corresponding to 0 V while 7600 Hz is corresponding to -1.5 V. A frequency demodulation module is added to the circuit to convert frequency to voltage for sweeping voltage detection. This frequency demodulation mechanism enables MoboSens to break through the limitations of different types of smart phones without considering the different speaker volume settings. Since it is common to have some drift within FM chips and resistors, a variation of the order of 25 mV is expected when converting frequency values to voltages. The cyclic sweeping voltage is then added to reference potential and working electrode is connected to ground which

makes the input voltage between working and reference electrode varying from 0 V to -1.5 V and back to 0 V. Although the sweeping range could be -1.6 V to $+1.5$ V, positive potential is avoided in case of oxidation of silver working electrode. Integrated operational amplifiers are used in circuit as potentiostat and a trans-impedance circuit is applied to convert the current to voltage. Since the frequency of this output voltage is low (which is below the detection limit of mobile phone microphone) and the amplitude is higher than the detection limit of the microphone input, a frequency modulation (FM) module is added to the circuit to convert the sensing data to the signal with the allowed frequency range of microphone jack.

2.5. Software implementation

The software is operated on Samsung make mobile phone with Windows Phone 7.5 OS (Android and iOS applications has also been developed; here, as an example, we describe Windows-based applications). The structure of software application is provided in S.1. There are three layers from low to high, which are the basic functions provided by Microsoft, sensor API (Application Programming Interface) and user interface. The sensor API is the core of this platform, which packages functions provided by Microsoft and is called by users' commands. In the user interface, there are four basic functions, namely, start, sensing, display and stop. Start function enables the sweeping voltage to drive the nitrate sensor; it also provides library of waveforms. Sensing function is mainly used to retrieve data from the output of nitrate sensor, and to analyze data including FM demodulation, down sampling and calibration. Display function is used for plotting the results for visualization. Stop function can be used for terminating these functions during operation.

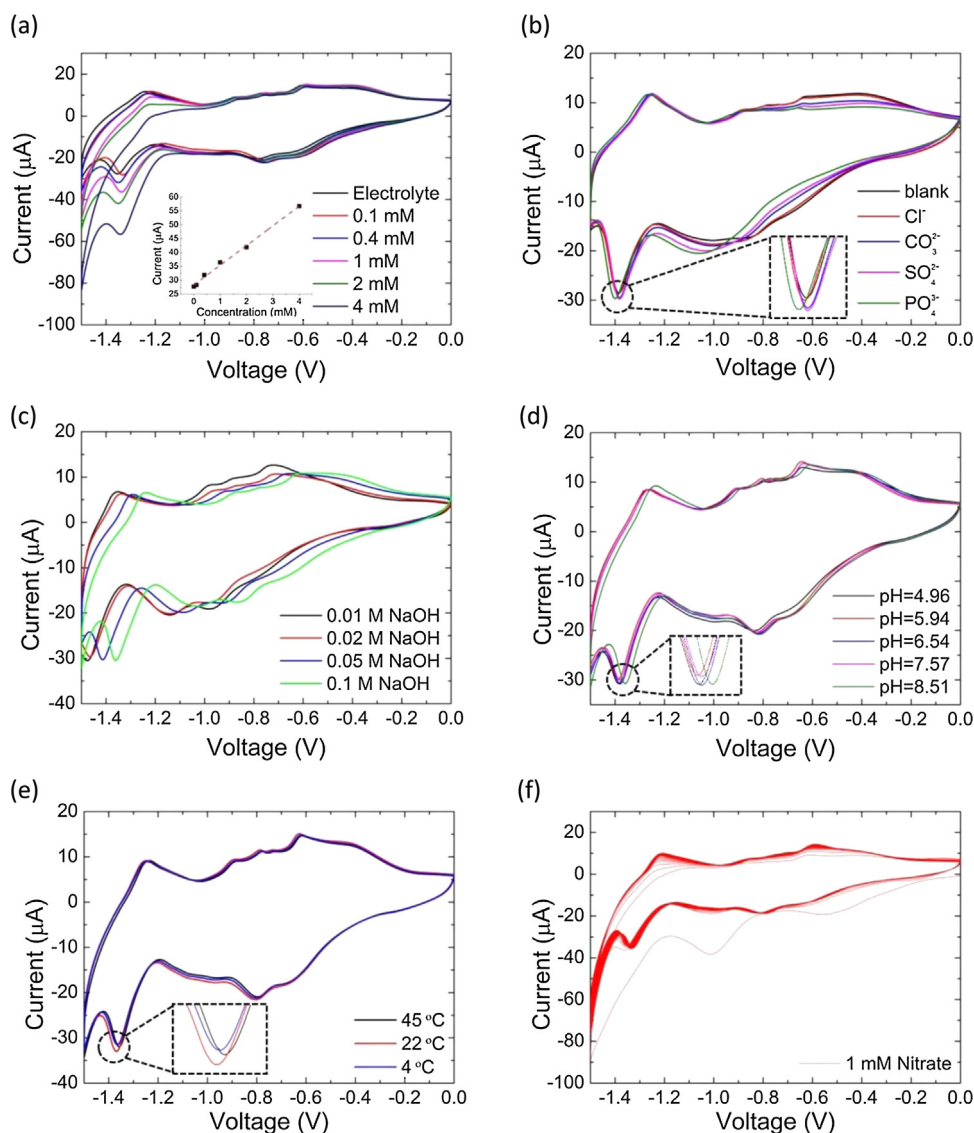


Fig. 4. Characterization of miniaturized sensor. (a) Raw data and calibration curve of standard nitrate solution (0.1 mM to 4 mM) using commercial potentiostat. The electrolyte (NaOH) concentration is 100 mM. (b) Effect of interfering ions: separate tests were performed by mixing NaCl (0.25 mM), Na₂CO₃ (0.25 mM), Na₂SO₄ (0.25 mM) and Na₃PO₄ (0.25 mM) solution to nitrate standard solution of 0.25 mM. The electrolyte (NaOH) concentration is 100 mM. (c) Effect of electrolyte concentration: cyclic voltammetry for 1 mM nitrate standard solution at different electrolyte (NaOH) concentrations (pH value: 12 to 13). (d) Effect of pH of the test solution: cyclic voltammetry for 1 mM nitrate standard solution at simulated soil water pH environment showing little effect of solution pH on the reduction peak position. The electrolyte (NaOH) concentration is 100 mM. (e) Effect of temperature of the solution: 1 mM standard nitrate solution was tested under different temperature with 100 mM electrolyte (NaOH). (f) Stability of sensor: cyclic voltammetry testing was performed for multiple times (100 times). The sweeping rate for cyclic voltammetry method above is 100 mV/s.

2.6. Data processing

Since the raw data recorded by mobile phone platform is a series of square waves at different frequencies from the FM integrated circuit (CD4046), averaging of frequency data over a window is performed to obtain the raw data. The FM property of CD4046 was first characterized. Then a calibration method is employed to transform the frequency values to voltage values. The sampling rate of cell-phone is 32000 bytes/s and each voltage value is stored as a short integer, so 16,000 data are recorded each second. The output from CD4046 is a square wave with amplitude larger than 0.7 V, but the input/output to the microphone inside Windows phone is limited to 200 mV (this value will differ for different make of phones). Hence, the recorded wave is a truncated square wave with maximum and minimum values of ± 32767 (2^{15} for signed short integer with 16 bits), respectively. Frequency value is calculated by counting the number of steps from maximum to minimum by setting

1600 samples as one period. Calibration is performed to convert the output frequency from the frequency modulation integrated circuit into voltage and finally to oxidation-reduction current using trans-impedance circuit. Based on the frequency modulation module, the relation between current and frequency follow equation (1):

$$\text{Current(A)} = \frac{(\text{frequency(kHz)} \times 0.5627 + 0.3552 - 4.1)(\text{V})}{\text{resistor}(\Omega)} \quad (1)$$

2.7. Modular integration of the sensor to mobile platform

The final packaging of the sensor is required for two reasons: portability and easy handling. In order to fulfill portability, a small circuit box was made attached with a light fixture frame fabricated using rapid prototyping manufacturing process. The fixture mechanism will make the circuit box stable when attached to a mobile phone. For ease in handling, a microfluidic chamber made up of

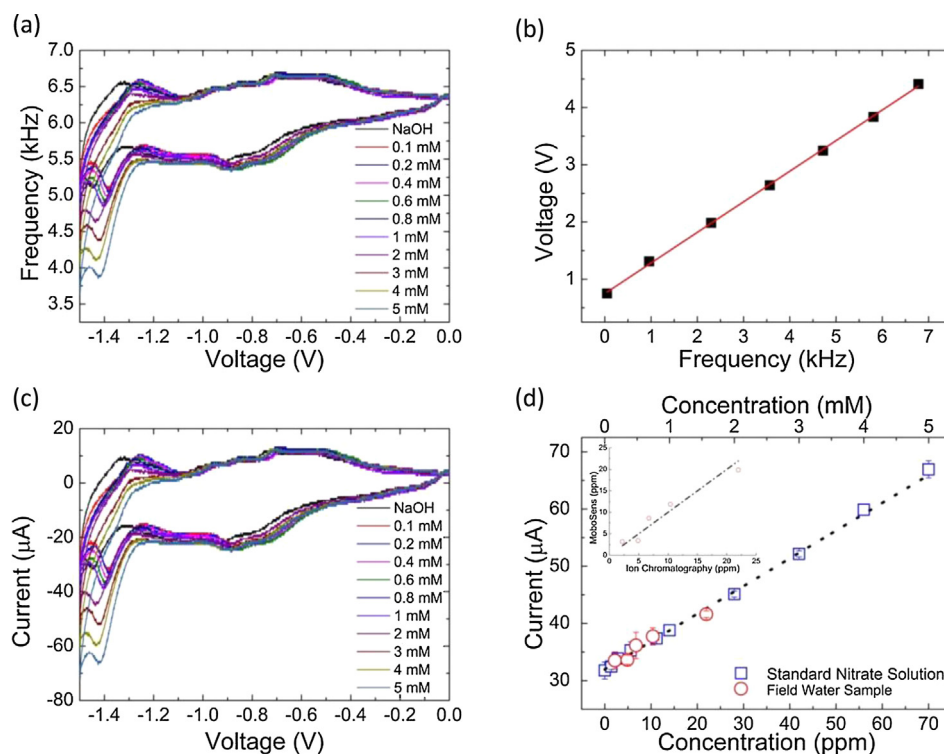


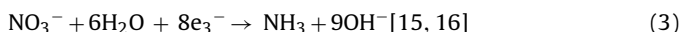
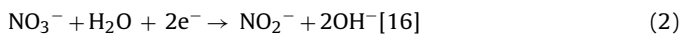
Fig. 5. Measuring nitrate using MoboSens. (a) Raw data from MoboSens platform as frequency values. (b) Calibration curve of CD4046 to convert frequency values to voltage. (c) Cyclic voltammetry testing of standard nitrate solution at 0.1 to 5 mM (1.4 to 70 ppm $\text{NO}_3\text{-N}$) using MoboSens platform at a scan rate of 100 mV/s. (d) Measurement of nitrate concentration in field water sample using MoboSens platform. For comparison, the field sample data are shown directly on the calibration curve obtained from standard nitrate solution shown in (c). Inset of (d) is the MoboSens deviation from ion chromatography data by fitting experimental data into calibration curve. The electrolyte (NaOH) concentration is 100 mM.

PDMS is used. The microfluidic chamber was made hydrophilic by exposing it to oxygen plasma for 1 min and was bonded to the active region of the electrochemical sensor on the glass slide. The volume of the microfluidic chamber is about 7 μL . By virtue of the capillary design of the test chamber, the sample liquid will be automatically dragged into the microfluidic chamber by capillary action, when a sample is placed at the sensor opening to perform testing.

3. Results and discussion

3.1. Miniaturized nitrate sensor characterization

Nitrate reduction in alkaline media is either two electrons (94%) or eight electron (6%) process as given below:



Standard testing samples with different nitrate concentrations from 100 μM (1.4 ppm $\text{NO}_3\text{-N}$) to 4000 μM (64 ppm $\text{NO}_3\text{-N}$) were first measured by a commercial potentiostat (CHI600) with a sweeping rate of 100 mV/s. The reduction current peaks were found around -1.35 V in Fig. 4(a), which shows a linear relationship with concentration. The fact that the peak potential is more negative compared with previous experiments from other research groups [15,16,35,36] can be attributed to more positive standard reduction potential of the reference electrode. This current peak is caused by the reduction of nitrate since the peak value increases with the increase of nitrate concentration. Since we used silver (Ag/Ag^+) as our reference electrode which acts as a pseudo reference electrode (not ideally nonpolarizable electrode), it showed modest drift (about 20 mV) at higher concentration of nitrate [18]. In order to quantify the effect of interference on nitrate detection due to

common soluble anions like chloride, carbonate, sulfate and phosphate, the interfering ionic solution were mixed with the nitrate standard solution. Nitrate standard solution with a concentration of 250 μM was mixed with chloride, carbonate, sulfate and phosphate at the same concentration respectively. Fig. 4(b) shows the similar location (-1.4 V to -1.38 V) for nitrate reduction peak, with a coefficient of variation (COV) of only 0.4%, which means the measurement is not interfered much by those interference ions. The COV is calculated by taking ratio of standard deviation and the mean value. We found that the COV for the magnitude of reduction peak current is only 1.7%, which indicates the accuracy of the sensor for measuring nitrate. This indicates the material of working electrode (Ag) and the strongly alkaline environment shows higher selectivity to nitrate reduction.

The effect of electrolyte concentration was characterized by mixing nitrate standard solution of same concentration to the sodium hydroxide solution at different concentrations. In Fig. 4(c), the positions of nitrate reduction current peak shifts from -1.35 V to -1.45 V while decreasing the concentration of sodium hydroxide from 0.1 M to 0.01 M. The main reason for such shift could be due to the increase of uncompensated resistance (R_u) between working and reference electrode as the electrolyte concentration is decreased by ten times [19]. So we keep the electrolyte concentration at 0.1 M to keep the reduction peak away from the sweep turning point (-1.5 V) for accuracy. Different pH value may also have some effect on the potential shift. Since the nitrate reduction process is irreversible [34], the peak potential E_p where the peak current is could be expressed in theory as [19]: $(4)E_p = E^{0'} - \frac{RT}{\alpha F} \left[0.780 + \ln \left(\frac{D_0^{1/2}}{K_0} \right) = \ln \left(\frac{\alpha F v}{RT} \right)^{1/2} \right]$ $E^{0'}$ is the formal potential of an electrode; R is gas constant; T is temperature; F is the Faraday constant; α is transfer coefficient; v

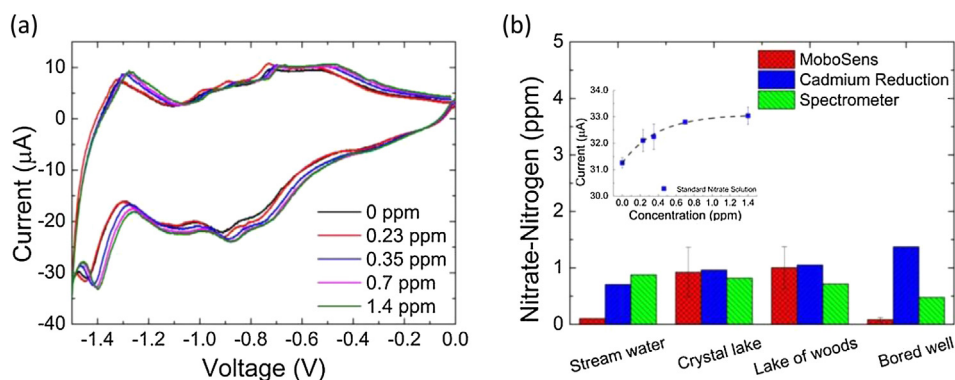


Fig. 6. Limit of detection of MoboSens platform. (a) Cyclic voltammetry testing for standard nitrate solution at sub-ppm concentration using MoboSens platform at a scan rate of 100 mV/s. (b) Comparison of different analytical methods to measure nitrate concentration in environmental water sample. The electrolyte (NaOH) concentration is 100 mM.

is voltage sweeping rate; D_0 is diffusion coefficient of oxidant; K_0 is the standard heterogeneous rate constant. It has been reported that the diffusion coefficient will increase with the decrease of pH value of the solution, especially with significant slope at low and high pH environment [37]. This can help explain the negative shift of peak potential shown in our experiments.

Further experiment was implemented to simulate the effect from soil water at different pH levels. Standard pH solutions containing same amount of nitrate varying from “very strong acid” (pH 4.5–5.0) to “strongly alkaline” (pH 8.5–9.0) [38] were dragged separately into micro-fluid chamber where sodium hydroxide solution at 0.1 M was pre-dried inside. Fig. 4(d) shows about 30 mV positive shift of peak potential as the pH value increases, which indicates a wide coverage of MoboSens platform for soil water at different pH levels.

The temperature effect was also determined by adding nitrate solution at 1 mM from environment under 45 °C, 22 °C and 4 °C, respectively in Fig. 4(e). The coefficient of variation (COV) is within 2%, which indicates temperature has little effect on the nitrate reduction current peak position.

Finally, repeatability of the miniaturized electrode was characterized by running cyclic voltammetry 100 times in nitrate solution at 1 mM in Fig. 4(f). The nitrate reduction peak current began to stabilize after the 4th cycle. By analyzing data from the 5th, 40th and 80th cycle, the COV was found to be 1.5%, which indicates this platform could be used for repeatable testing.

3.2. Measurement on MoboSens platform

Sodium nitrate solutions at different concentration (100 µM (1.4 ppm NO₃-N) to 5 mM (70 ppm NO₃-N)) with 0.1 M NaOH electrolyte medium were tested by the MoboSens platform. Fig. 5(a) shows the recorded frequency changing with sweeping voltage (Raw data in S.2). The frequency values were converted to voltage first, by using the linear voltage to frequency relationship shown in Fig. 5(b). The current values were then calculated by dividing the resistance value of the resistor where the current pass through and shown in Fig. 5(c). During the forward sweeping process (0 V to –1.5 V), there are current peaks which occur at around –1.35 V to –1.4 V. The magnitude of the reduction current peaks is dependent on the concentration of nitrate present in the solution. The position of the reduction peak shifts about 50 mV to more negative value as the concentration of nitrate increases. This shift could be due to the existence of uncompensated resistance (R_u). Unlike commercial potentiostat which has a good control of $E + iR_u$ between working and reference electrode (E is the potential applied to working electrode); we controlled the true potential applied on working electrode. The practical effect of uncompensated resistance is to

shift the reduction peak toward more negative potentials, especially in higher scan rate and higher concentration conditions which cause larger reduction current [19]. The small wide peaks around –0.9 V could be attributed to hydroxide desorption process on silver electrode [15,39]. In the anodic sweeping process, an anodic current peak occurs at around –1.25 V, which is due to the electro-chemisorption of hydroxide ions [36,39].

The calibration curve is obtained from the current reduction peak values after data processing in Fig. 5(d). With linear fitting method, calibration equation could be written as:

$$\text{Current(A)} = -4.8506 \times 10^{-7} \text{ Concentration(ppm)} - 4.3973 \times 10^{-5} \quad (5)$$

The relation between reduction current and concentration shows linearity within the concentration range in 100 µM (1.4 ppm NO₃-N) to 5 mM (70 ppm NO₃-N). The blue data points in Fig. 5(d) are measurement from standard nitrate solution while red data points are measurement from field water samples provided by Department of Agriculture at University of Illinois. The statistical error bar is based on four testing results using the same concentration. For the standard nitrate solution, samples with low concentration (~2 ppm) show larger standard deviation compared with samples having higher concentration of nitrate. Since there is always oxygen dissolved in solution, the deviation from linearity could be due to oxygen reduction. This reaction interferes with nitrate measurement by taking place at a more positive potential than nitrate reduction [15,34]. We anticipate this effect will be more pronounced at lower concentration of nitrate (<2 ppm), and hence, will not challenge the reliability of sensor to measure nitrate at higher concentration (>2 ppm).

3.3. Field water sample testing

The field water samples are first filtered using a 0.1 µm Whatman filter paper to remove the suspended particles. For comparison, the concentrations of nitrogen in nitrate were measured by Dionex Ion Chromatography with a detection limit of 0.08 ppm. Fig. 5(d) shows nitrate concentration of field water samples (red circle) measured by MoboSens platform and compared them with the calibration curve obtained with nitrate standard solution (blue square). The inset of Fig. 5(d) shows the comparison of MoboSens results with that of Ion Chromatography measurement for the same field water samples. The measurements are within ±15% deviation at low concentration (2.2 ppm) and ±5% deviation at high concentration (22 ppm). This verifies the ability of MoboSens platform to perform farm based field water testing.



Fig. 7. User interface and network connection of MoboSens app. (a) Front page of the app. (b) Testing results plotted on the phone screen. (c) Interface showing the ability to input user “metadata”, along with the ability to pull publicly available data (e.g. USGS weather data) and showing them in one map. (d) Bing map interface with the current location of experiment shown on the map. (e) Message posted on Twitter website through the MoboSens platform. (f) Satellite view of recently posted data.

3.4. Environmental water testing

In addition to the field water sample, MoboSens was utilized to measure nitrate concentration in environmental water samples. By adjusting the trans-impedance from 20 k Ω to 100 k Ω , the detection limit could be pushed to more diluted nitrate solution (around 10 μ M (0.14 ppm)). The principle of trans-impedance is to convert current to voltage and voltage is converted to frequency as mentioned earlier. This adjustment is to fit a lower concentration range into a wide frequency range. Fig. 6(a) shows the results of standard nitrate solution with low concentration (less than 1.4 ppm) (raw data in S.4). The reduction current peaks are calibrated in Fig. 6(b). Testing was then performed for environmental water samples. These water samples were collected from different sources like lakes, streams and local wells. The raw data was processed with the method described in previous section and the peak current was fitted into the calibration equation (raw data in S.5). To verify the accuracy of measurement results obtained using this mobile sensor platform, methods like cadmium reduction and ultraviolet (UV) absorption spectroscopy were performed for comparison [34]. The cadmium reduction method was based on the reduction of nitrate to nitrite on cadmium as a catalyst, followed by Griess reaction to form a fluorescent chemical. Cadmium reduction method is normally considered the “gold standard” for the detection of nitrate level. The UV absorption spectroscopy method was performed by scanning wavelength in a range from 190 nm to 450 nm. Nitrate concentration was calibrated from the absorption spectrum at different concentrations. The comparison of nitrate concentration of different water samples after calibration using the three different methods is shown in Fig. 6(b).

From the results, the coefficient of variation (COV) of nitrate concentration in crystal lake and lake of the woods with respect to cadmium reduction method is 4.1% and 4.7%, respectively. The concentration of nitrate ion tested by MoboSens from these two water sources is consistent with the cadmium reduction method. Water from streams and bored well shows much lower concentration in MoboSens compared to other methods, especially a large COV with respect to cadmium method. The large COV is attributed to presence of nitrite in the sample as cadmium reduction methods convert nitrite into nitrate first and then measure the total nitrogen. Above all, the nitrate concentrations of all water samples were far below 10 ppm, which satisfied the requirements for water safety prescribed by EPA.

3.5. Network integration to the nitrate sensing

The application on windows phone is further developed to integrate the location of testing (longitude and latitude) to the nitrate sensing and displayed it on Bing maps. The temperature data is also included in the nitrate sensing. The phone application also enables users to add any metadata (such as user comments and graphics) along with the shared nitrate sensing information provided by the user. User has the option to send this sensing data to social network sites such as Twitter for public dissemination or upload to secure cloud server for further analysis. An example of the developed phone application interface is given in Fig. 7. Fig. 7(a) shows the main page of application. Fig. 7(b) displays a plot from a testing result. In the interface showed in Fig. 7(c), users will be able to send metadata along with the testing results. Fig. 7(d) shows the location of the performed test on a Bing Map. After sending

metadata to Twitter, a message about nitrate information could be seen posted on Twitter website, as showed in Fig. 7(e). Fig. 7(f) shows the satellite view of the location where testing is performed with nitrate information labeled.

4. Conclusions

In summary, we have demonstrated an audio jack-based mobile sensing system for rapid and real-time nitrate concentration measurement. It contains a microfabricated three-electrode sensor, a mobile application and a circuit board developed for communicating with the sensor. The mobile sensing platform was used to test nitrate ion in field water as well as environmental water samples and compared with existing analytical testing methods. The mobile platform based sensing was found to be comparable with the traditional sensing methodology. Finally, the measured concentration value, location of testing site and metadata such as user inputs are communicated and shared at social network websites and secured cloud server for further analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2014.12.017>.

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